REMOVAL OF ANIONIC SURFACTANTS FROM WASTEWATER BY MAGNETIC MINERAL SORBENTS

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Abstract. The simplest and most effective method of removing low concentrations of anionic surfactants such as sodium dodecyl benzensulphonate (SDBS) and sodium lauryl sulfate (SLS) is adsorption. Among adsorbents the natural clays are cheap and promising for these purposes. However, there are significant difficulties in removal of spent sorbent after the adsorption process. So, the creation of magnetic sorbents that can be effectively removed from water after sorption by magnetic separation will be a successful decision. The aim of this investigation is the creation of cheap and efficient magnetic sorbents based on natural clays and magnetite for anionic surfactant removal from wastewater. We have synthesized a series of magnetic sorbents from different natural clays with a content of magnetite from 2 to 10 wt%. The ability of magnetic sorbents to remove SDBS and SLS from aqueous solutions has been studied for different adsorbate concentrations by varying the amount of adsorbent, temperature and shaking time. Thermodynamic parameters were calculated from the slope and intercept of the linear plots of ln K against 1/T. Analysis of adsorption results obtained at different temperatures showed that the adsorption pattern on magnetic sorbents correspond to the Langmuir isotherm. It is shown that with increasing the content of magnetite in the magnetic sorbents improves not only their separation from water by magnetic separation, but adsorption capacity to SDBS and SLS. Thus, we obtained cheap magnetic sorbents based on natural clays and magnetite by the easy way, which not only quickly separated from the solution by magnetic separation, but effectively remove anionic surfactants.

Keywords: adsorption, anionic surfactant, magnetite, magnetic separation, magnetic sorbent, natural clay.

Introduction

World production of surfactants (SAs) is growing by reason permanent increase of their use. SAs are widely used in industry, agriculture, medicine and everyday life. The major fields of SAs consumption are the detergents production for technical and hygiene requirements and manufacturing of necessary substances for the processing of fabrics, leather and paintwork products (Pal et al., 2013).

SAs contaminate water bodies mainly. More than 100 thousands of SAs are annually emitted into the water by chemical plants (Mortazavi, Faramany, 2015). Maximum permissible concentration of SAs in the water of natural reservoirs is 0.5 mg/l (Klimenko, Tymoshenko, 1993).

SAs are strong carcinogenic agents. Products of their decay are toxic and can accumulate in the body and cause irreversible pathological changes (Ebrahimi et al., 2015). In addition, SAs slow down disintegration of other carcinogens and inhibit the biochemical processes of oxygen consumption and nitrification. Therefore, necessity of wastewater treatment from SAs is obvious (Amiranshoja et al., 2013).

The study (Kyzas et al., 2013) showed that the synthetic akaganeite is effective mineral sorbent for removal of different SAs. The maximum adsorption capacity was 823.96 mg/g for sodium dodecyl sulfate, 1007.93 mg/g for cetyltrimethylammonium bromide, and 699.03 mg/g for “Tween 80”. Needed efficiency wastewater decontamination requires the use synthetic nanosized akaganeite obtained by co-precipitation. High raw material cost and duration of the sorbent synthesis questions the appropriateness of its use from the economic point of view.

The natural zeolite (Nord Kochba, Armenia) was used as a sorbent for the removal of cationic and anionic SAs (Harutyunyan, Pirumyan, 2015). Sorption capacity of zeolite relatively anionic surfactant was significantly lower (113 mg/g) compared to cationic surfactant (284 mg/g). Furthermore, the duration of sodium dodecyl sulfate removal with 99 % efficiency from aqueous solution was more 170 minutes. This means that wastewater treatment from SAs by zeolites requires more duration of the process, which is unacceptable in the large scale implementation.

Fast enough sodium dodecyl sulfate removal from water environment occurs by aluminum oxide adsorption, since the maximum sorption capacity of 197.7 mg/g is achieved was already for 1 hour (Priti, Hemangi, 2012). These results were achieved in the surfactant sorption from highly concentrated solution (200 mg/l) which is not typical for real wastewater.

Adsorption of three different nature SAs such as Triton X-100 (non-ionic), sodium dodecylsulphate (anionic) and octadecyltrimethylammonium bromide (cationic) by four layered (montmorillonite, illite, muscovite and kaolinite) and two non-layered (sepiolite and palygorskite) clay minerals was studied (Sanchez-Martin et al., 2008). The adsorption of non-ionic and cationic SAs was higher by montmorillonite and illite, and for anionic sur-
factant was found that adsorption was above kaolinite and sepiolite. So, the use of clay minerals mixture was suggested for disposal of wastewater contaminated with SAs.

Thus, the use of natural minerals for wastewater treatment from SAs is advisable if clays have low cost, high sorption capacity; they are available. Apart this, clay must quickly remove surface-active substances from the low concentrated wastewater. Besides, the use of clay minerals causes the appearance of significant difficulties in removing waste sorbent particles from solution after the sorption process due to their high dispersity.

Order to overcome such difficulty proposed to create composites based on clay mineral in combination with magnetite (Mykhailenko et al., 2015). The suggested technology envisages the using of nanosized Fe₃O₄ as nanosorbent or modifier for improving the efficiency of removal of pollutions (Makarchuk et al., 2016).

So, in this paper, the combining of adsorption properties of clay minerals (saponite, spondey clay and palygorskite) and magnetic properties of magnetite (Fe₃O₄) is proposed for obtain efficient magnetic composite adsorbents. The advantage of magnetic composite sorbents (MCS) is the ability of removing from the aqueous medium by simple magnetic separation procedure after setting sorption equilibrium.

The sorption, kinetic and thermodynamic laws of SLS and SDBS removal from aqueous solutions by clay minerals, magnetite and composite sorbents based on them were investigated.

Materials and Methods

Sample preparation

All of MCS samples were produced by impregnation method. Saponite, spondey clay, palygorskite (particle size less than 230 meshes (63 μm)) and magnetic fluid was stirred for 30 minutes for Fe₃O₄ adsorption on the clay surface. Magnetic fluid was synthesized by known method Elmore (Thach et al., 2008). The received suspension was separated in the magnetic filter and dried at a temperature of 60-80 °C within 24 hours. Thus, samples of magnetic sorbents based on saponite (MCSp-2, MCSp-4, MCSp-7, MCSp-10), spondey clay (MCStd-2, MCStd-4, MCStd-7, MCStd-10) and palygorskite (MCP-2, MCP-4, MCP-7, MCP-10) containing 2 wt.%, 4 wt.%, 7 wt.% and 10 wt.% of magnetite were obtained.

Adsorption kinetic

The 1 g of sorbent sample (clay, magnetite and composite on their basis) were put in contact with 100 ml of anionic surfactant solution with an initial solution concentration of 100 mg/L. The experiment was carried out by batch adsorption method. The assays were conducted for a period of 15, 30, 60, 120 and 180 min at temperature 20±2 °C using a flash shaker at 350 rpm. After the expiry of the specified time suspension was centrifuged at 3000 rpm for 5 min and residual (equilibrium) concentration of anionic SAs in the sample was measured by direct two-phase (2P) titration of cationic surfactant in the layer of chloroform (Schmitt, 2001).

Adsorption procedure

Study of sorption properties of sorbent samples was performed by batch adsorption. The 1 g sample of sorbent was brought to a round bottom flask filled with model test of water in volume of 100 ml. Standard solutions of 5, 10, 50, 100, 250, 500 and 1000 mg/l SDBS and SLS were prepared for isotherms investigation. The resulting suspension was stirred in a shaker for 1 hour with speed of 350 rpm. After setting of adsorption equilibrium the suspension was separated in a field of centrifugal forces during 5 minutes at 3000 rpm. The resulting liquid phase was used to determine the equilibrium concentration of anionic SAs according to the method of direct two-phase (2P) titration analysis presented in the section Adsorption kinetic Materials and Methods.

The value of organic pollutants adsorption from water systems can be calculated:

\[ a = \frac{x}{m} \]  \hspace{1cm} (1)

where \( a \) is adsorption of \( x \) mg of surfactant per \( 1 \) g of sorbent, mg/g; \( x \) is amount of adsorbed surfactant from 100 ml of solution (adsorption index), mg:

\[ x = \frac{(C_0 - C_1) \cdot 100}{1000} \]  \hspace{1cm} (2)

where \( C_0 \) and \( C_1 \) is initial (\( C_0 = 100 \) mg/l) and equilibrium concentration of surfactant in model solution respectively, mg/l.

Adsorption kinetic parameters

In the process of surfactants removal from sewage sorption kinetics is important to select the optimal conditions of water purification. It provides important information about the ways and mechanisms of sorption. As is well known, sorption process is complicated and multistage therefore traditional kinetic models are not always suitable to describe complex adsorption treatment. In this regard, to describe the sorption kinetics in modern scientific literature (Günay et al., 2013; Hernandez et al., 2013; Elmoubariki et al., 2015) the kinetic model of the pseudo-first order, pseudo-second order model and diffusion Boyd-Adamson model are used, which reveal the influence of the chemical stage.

The pseudo-first order model of speed is the earliest sorption kinetics model and is represented in the form (Günay et al., 2013; Hernandez et al., 2013; Elmoubariki et al., 2015):

\[ \frac{dQ}{dt} = k_1 \left( Q_{(t)} - Q \right) \]  \hspace{1cm} (3)

where \( Q_{(t)} \) and \( Q \) is sorption capacity of surfactant at equilibrium and at time \( t \), mg/g; \( k_1 \) is pseudo-first order model rate constant, 1/min.

Equation (3) in the integration of boundary conditions from \( t = 0 \) to \( t = t \) and \( Q_0 = 0 \) from to \( Q = Q_1 \) takes the following form:
\[
\ln \left( Q_{(e)} - Q \right) = \ln(Q_{(e)}) - \frac{k_t}{2.303} \cdot t,
\]

where \( Q_{(e)} \) and \( Q \) is calculated as follows:

\[
Q = \frac{(C_s - C_r) \cdot V}{m} \cdot 1000,
\]

where \( C_s \) and \( C_r \) is initial surfactant concentration and concentration of surfactant in solution at time \( t \), respectively, mg/l; \( V \) is model solution volume, l; \( m \) – mass of sorbent sample, g.

For description of sorption process in aqueous solution pseudo-second order model of speed is also used (Günay et al., 2013; Hernandez et al., 2013; Elmoubarki et al., 2015):

\[
\frac{dQ}{dt} = k_2 \cdot \left( Q_{(e)} - Q \right)^2,
\]

where \( k_2 \) is pseudo-second order rate model constant, g/(mg·min).

The integrated form of the classical rate equation of pseudo-second order model looks like:

\[
Q = \frac{t}{k_2 \cdot Q_{(e)}^2 + \frac{t}{Q_{(e)}}}.
\]

The analysis of primary kinetic curves was conducted using the equation for Boyd-Adamson internal diffusion kinetics model (Krizhanovskaya et al., 2014):

\[
F = \frac{\theta}{\theta_e} = 1 - 6 \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left( \frac{-D \cdot \pi^2 \cdot n^2 \cdot t}{r^2} \right),
\]

where \( \theta \) and \( \theta_e \) is the degree of saturation of sorbent after \( t \) seconds and infinite time, respectively; \( F \) is the degree of equilibrium achievement; \( D \) is the diffusion coefficient, sm²/s; \( r \) is sorbent particle radius, mm; \( n \) is number of integers 1, 2, 3, 4, 5.

Criterion of Fourier:

\[
\frac{D \cdot \pi^2 \cdot t}{r^2} = Bt,
\]

where \( B \) is the rate constant of diffusion, that is:

\[
B = \frac{D \cdot \pi^2}{r^2}.
\]

Substituting the (9) into the equation (8) has received to:

\[
F = 1 - \frac{6}{\pi} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left( -Bt n^2 \right),
\]

where \( Bt \) is the dimensionless parameter, which is the solution of task of diffusion in the solid part.

For experimentally obtained values of \( F \) by the table of Attachment 3 on the page 194 (Polyansky et al., 1976) the appropriate value of \( Bt \) is determined. To confirm the diffusion limiting sorption process the construction of \( Bt \) versus \( t \) and \( -\ln(1-F) \) versus \( t \) are used. The linear dependence \( Bt \) on \( t \) evidences in favor of limiting internal diffusion. Linearity depending \( -\ln(1-F) \) on \( t \) can point to external diffusion mechanism or adsorption kinetics.

If dependence \( Bt = f(t) \) is linear the limiting stage of adsorption treatment is diffusion in sorbent phase. Slope of this line is equal to \( B \), and then the average diffusion coefficient in the sorbent particle is, sm²/s:

\[
D = \frac{B \cdot r^2}{\pi^2}.
\]

**Adsorption isotherms**

Adsorption isotherms describe the relationship between the adsorbate and adsorbent. The obtained isotherms were analyzed using four models including Langmuir, Freundlich, Temkina and Dubinin-Radushkevycha isotherms. Langmuir adsorption isotherm quantitatively describes the formation of a monolayer of adsorbate on the external adsorbent pores surface. The model assumes equal adsorption energy on the surface of the sorbent. Based on these assumptions, the Langmuir model in the linear form is represented by the equation (Dada et al., 2012):

\[
\frac{1}{Q_{(e)}} = \frac{1}{Q_s} + \frac{1}{Q_s \cdot K_L \cdot C_{(e)}},
\]

where \( C_{(e)} \) is equilibrium concentration of surfactant, mg/l; \( K_L \) is constant of Langmuir equation, 1/mg.

Freundlich adsorption isotherm is used to describe adsorption on heterogeneous surfaces. According to this model adsorption centers different energies of interaction. Since active centers with maximum energy are saturated primarily. The linear form of Freundlich model is described by equation (Dada et al., 2012):

\[
\log Q_{(e)} = \log K_f + \frac{1}{n} \cdot \log C_{(e)},
\]

where \( K_f \) is Freundlich equilibrium constant, mg/g; \( 1/n \) is parameter that indicates the intensity of interaction between adsorbent and adsorbate.

The Temkin model takes into account the interaction between adsorbent and adsorbate. The model assumes that the heat of molecules adsorption in the layer will decrease linearly, not logarithmic with increasing degree of filling surface.

The Temkin model in the linear form is as follows (Dada et al., 2012):

\[
Q_{(e)} = B \cdot \ln A_T + B \cdot \ln C_{(e)},
\]

\[
B = \frac{RT}{b_T},
\]

where \( A_T \) is Temkin equilibrium constant, l/g; \( b_T \) is Temkin equations constant, l/g; \( B \) is constant of adsorption heat, J/mol.

Dubinin-Radushkevich isotherm is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface (Elmoubarki et al., 2015). The model has often success-
fully fitted high solute activities and the intermediate range of concentrations data well:

\[ \ln Q_{(e)} = -\beta \cdot \varepsilon^2 + \ln Q_{(e)} \], \hspace{1cm} (17)

where \( \beta \) is Dubinin–Radushkevich equilibrium constant, \( \text{mol}^2 \text{kJ}^{-2} \); \( \varepsilon \) is the Polanyi potential.

This approach was usually applied to distinguish the physical and chemical adsorption of organic pollutants. Its mean free energy per molecule of adsorbate (for removing a molecule from its location in the sorption space to the infinity) can be computed by the relationship:

\[ E = \frac{1}{\sqrt{2\beta}} \], \hspace{1cm} (18)

where \( \beta \) is denoted as the isotherm constant.

Meanwhile, the parameter \( \varepsilon \) can be calculated as:

\[ \varepsilon = RT \cdot \ln(1 + \frac{1}{C_{(e)}}) \]. \hspace{1cm} (19)

### Adsorption thermodynamic

The 100 ml of surfactant model solution of 100 mg/l concentration was mixed with 1 g of sorbent sample. The resulting suspension was thermostatic controlled at 290, 323, 343 K and stirred for 60 minutes using a flash shaker at 350 rpm. After the expiry of the above time sorbent was separated by centrifugation at 3000 rpm for 5 min and the residual (equilibrium) concentration of surfactant was identified.

Thermodynamic parameters, like heat of sorption \( \Delta H^0 \), entropy \( \Delta S^0 \), and free energy of activation \( \Delta G^0 \), play an important role in predicting the adsorption behavior because these are strongly dependent on temperature. From the following equation, it is possible to calculate the Gibbs energy changes for the adsorption process at different temperatures (Elmoubarki et al., 2015):

\[ \Delta G^0 = -RT \cdot \ln K_D, \] \hspace{1cm} (20)

where \( R \) is the gas constant, \( K_D \) is equilibrium constant at the temperature \( T \).

The numerical values of the equilibrium constant were calculated from:

\[ K_D = \frac{C_{be}}{C_{ae}} \], \hspace{1cm} (21)

where \( C_{be} \) and \( C_{ae} \) are the equilibrium concentrations of SAs on adsorbent solid phase and in solution liquid phase, respectively, mg/l.

The free energy of activation \( \Delta G^0 \) can be calculated by the following equation:

\[ \Delta G^0 = \Delta H^0 - T \cdot \Delta S^0, \] \hspace{1cm} (22)

The enthalpy (\( \Delta H^0 \)) and entropy changes (\( \Delta S^0 \)) of the adsorption can be determined through the slope and intercept of the plot \( \ln K \) versus \( 1/T \) using Van’t Hoff equation (Elmoubarki et al., 2015):

\[ \ln K_D = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}, \] \hspace{1cm} (23)

where, \( R \) is the gas constant (8.314 J/(mol·K)), \( T \) is solution temperature (K) and \( K_D \) is the distribution coefficient of the surfactant between the adsorbed layer and the solution.

### Results

### Adsorption kinetic

Kinetic dependences of anionic SAs adsorption by clay minerals (saponite, spondyle clay, palygorskite), magnetite and composites on their base are shown in Figure 1.

### Isotherm data

Adsorption isotherms of SDBS (a, c, e) on clay minerals, magnetite and composites based on them are presented on Figure 2.

### Model fitting and kinetic parameters

In order to analyze the experimental data in terms of the adsorption kinetics a pseudo-first order, pseudo-second order model and diffusion model were used. The values of \( k_1 \), \( k_2 \), \( D \) and correlation coefficient (\( R^2 \)) for the studied cases are listed in Table 1.

### Table 1. Kinetic parameters and correlation coefficients of pseudo-first order, pseudo-second order and diffusion model of SDBS and SLS adsorption by magnetic mineral sorbents

<table>
<thead>
<tr>
<th>Kinetic model</th>
<th>Pseudo-first order model</th>
<th>Pseudo-second order model</th>
<th>Diffusion model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \ln(\frac{Q_{(e)}}{Q_{(e)}}) = f(t) )</td>
<td>( \frac{t}{Q_{(e)}} = f(t) )</td>
<td>( -\ln(1-F) = f(t) )</td>
</tr>
<tr>
<td>Sample</td>
<td>( k_1 ) ( R^2 )</td>
<td>( k_2 ) ( R^2 )</td>
<td>( R^2 )</td>
</tr>
<tr>
<td>SDBS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCSp-7</td>
<td>0.1036 0.9972</td>
<td>0.0040 0.9983</td>
<td>0.9972</td>
</tr>
<tr>
<td>MCSRd-4</td>
<td>0.0956 0.9990</td>
<td>0.0088 0.9959</td>
<td>0.9990</td>
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<tr>
<td>MCP-7</td>
<td>0.0599 0.7609</td>
<td>0.0049 0.9884</td>
<td>0.7609</td>
</tr>
<tr>
<td>SLS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCSp-7</td>
<td>0.0668 0.8225</td>
<td>0.0029 0.9501</td>
<td>0.8225</td>
</tr>
<tr>
<td>MCSRd-4</td>
<td>0.0544 0.5589</td>
<td>0.0088 0.9903</td>
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<td>MCP-7</td>
<td>0.0518 0.8364</td>
<td>0.0109 0.9915</td>
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</table>
Model fitting and adsorption isotherm parameters

The adsorption equilibrium data were analyzed using Langmuir, Freundlich, Temkin and Dubinin-Radushkevych adsorption models. The parameters of adsorption isotherms are compiled in Table 2.

Table 2. Adsorption isotherm parameters and correlation coefficient of SDBS and SLS adsorption by magnetic mineral sorbents

<table>
<thead>
<tr>
<th>Sample of surfactant</th>
<th>Langmuir Isotherm</th>
<th>Freundlich Isotherm</th>
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<tr>
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<td>---</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>$K_L$, l/mg</td>
<td>$Q_{ads}$, mg/g</td>
<td>$R^2$</td>
<td>$K_f$, mg/g</td>
</tr>
<tr>
<td>SDBS</td>
<td></td>
<td></td>
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<td>---</td>
<td>---</td>
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<tr>
<td>MCSp-7</td>
<td>0.9951</td>
<td>0.0265</td>
<td>38.7597</td>
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<td>1.0245</td>
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<td>0.7301</td>
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<td>MCP-7</td>
<td>0.9972</td>
<td>0.0183</td>
<td>52.0833</td>
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<td>0.7066</td>
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<td>SLS</td>
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<td>---</td>
<td>---</td>
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<td>Sorbent</td>
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</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>$K_L$, l/mg</td>
<td>$Q_{ads}$, mg/g</td>
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<td>$K_f$, mg/g</td>
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<td>MCSp-7</td>
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<td>---</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>$K_L$, l/mg</td>
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<td>$R^2$</td>
<td>$E$, kJ/mol</td>
</tr>
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Termodynamic parameters of adsorption

For the study of thermodynamics of anionic SAs removal the sorption process was investigated at temperature 293 K, 323 K and 343 K. Thermodynamic parameters were calculated from Van’t Hoff plots. The defined values of $\Delta H^o$, $\Delta S^o$, and $\Delta G^o$ for anionic SAs adsorption at different temperatures are given in Table 3.

Table 3. Thermodynamic parameters for SDBS and SLS adsorption by magnetic mineral sorbents

<table>
<thead>
<tr>
<th>Sample of surfactant</th>
<th>$T$, K</th>
<th>$\Delta G^o$, J/mol</th>
<th>$\Delta H^o$, J/mol</th>
<th>$\Delta S^o$, J/(mol·K)</th>
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<tr>
<td>SDBS</td>
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</tr>
<tr>
<td>MCSp-7</td>
<td>293</td>
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<td>323</td>
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Discussion

Adsorption kinetic

According to the kinetic dependencies of anionic SAs removal from aqueous solutions (Fig. 1) the equilibrium time was reached in 60 minutes for the all magnetic composites. The purification of water model solutions of SDBS and SLS by using clay minerals was lasted for 120 minutes and 60 minutes respectively. Moreover, the percentages of anionic SAs adsorption for magnetic composites were in 1.5-2.5 times higher compared with native natural clays. When magnetic fluid was used as a sorbent the sorption equilibrium was set relatively quickly, such as 30 minutes. But the degree of pollutants removal was low and amounted to 39.5 % for SDBS and 15.9 % for SLS.

Sorption equilibrium of anionic SAs removal by magnetic composites was achieved significantly faster compared to clay minerals illite, muscovite, kaolinite and sepiolite for which it was at least 24 hours (Sanchez-Martín et al., 2008).

Adsorption isotherm data

The maximum sorption capacity of MCSp, MCSd and MCP in the disposal of anionic SAs was in the range of 32-36 mg SDBS/g and 29-36 mg SLS/g, respectively (Fig. 2). The sorption capacities of native saponite, spondylite clay, palygorskite and for SDBS and SLS obtained from the sorption isotherms.
were in 2-4 and 2-7 times lower, respectively. Sorption capacity of magnetite proved comparatively low at 20.89 mg SDBS/g and 13.81 mg SLS/g. As can see from the Figure 2 the highest sorption capacity relatively SDBS was achieved using magnetic composites MCSp-7 (36.49 mg/g), MCSd-4 (38.39 mg/g) and MCP-7 (47.04 mg/g). The sorption capacity of MCSp-7, MCSd-4 and MCP-7 in relation to SLS removing was 35.70 mg/g, 34.79 mg/g and 32.1 mg/g respectively and was highest compared to other samples of sorbents. So, the magnetic composites MCSp-7, MCSd-4 and MCP-7 were selected for further research: for kinetic parameters calculations, to estimate the validity of experimental data with isotherm models and study of thermodynamics the sorption process.

Sorption capacity of sorbents in works (Kyzas et al., 2013), (Priti, Hemangi, 2012) and (Harutyunyan, Pirumyan, 2015) relatively anionic SAs are several times higher compared to the obtained magnetic composites. However, sorption properties of these materials were investigated in highly concentrated anionic SAs solutions with minimal initial concentration of 2000 mg/g. Thus, the obtained results do not guarantee the effectiveness of synthetic akaganeite, aluminum oxide and zeolite in real low concentrated wastewater. Moreover, investigated sorption materials are more expensive than composites based on natural clay minerals. In our case, the study was carried out at lower concentrations (maximum concentration of SDBS and SLS in model solutions was 1000 g/l).

Fig. 2. Adsorption isotherm of SDBS (a, c, e) and SLS (b, d, f) on sorbents samples
Thus in this study were provided conditions as close as possible to real. 

The maximum sorption capacities of magnetic composites containing magnetite 4-7 wt.% towards SDBS and SLS were in 4 and 7 times respectively higher compared to the native saponite, spondyle clay, palygorskite. Furthermore, sorption capacities of this magnetic sorbents exceeded the sorption capacity of magnetic fluid in 2 times. Thus, the synergistic effect was found and it was related, in our view, with change of porous structure of natural clay minerals and stabilization of Fe3O4 nanoparticles on their pores surface. The comparative analysis of porous structure saponite clays and magnetic composites based on it are given in the works (Makarchuk et al., 2015; Makarchuk et al., 2016).

Adsforption kinetic models

Dependences of sorption of SDBS and SLS by samples of sorbents MCSp-7, MCScd-4 and MCP-7 in the linearized coordinates of the pseudo-first order, pseudo-second order and diffusion were established.

The best adjustment of the process of anionic SAs extracting from aqueous solutions by magnetic composites MCSp-7 (for SDBS and SLS adsorption $R^2$ is 0.9983 and 0.9501, respectively), MCScd-4 (for SDBS and SLS adsorption $R^2$ is 0.9959 and 0.9903, respectively), and MCP-7 (for SDBS and SLS adsorption $R^2$ is 0.9884 and 0.9515, respectively) was to the pseudo-second order model. Based on the rate constants of pseudo-second order model $k_2$ values, the choice of magnetic composites mineral base was suggested. As follows, the SDBS and SLS removal occurred most intense with application of composites based on spondyle clay and palygorskite accordingly.

The kinetic data of anionic SAs sorption were analyzed by Boyd-Adamson diffusion kinetics model. The assumption about the possibility of limiting sorption process of purification in the internal diffusion field was confirmed. Calculated for SDBS and SLS adsorption onto MCSp-7, MCSd-4 and MCP-7 adsorption diffusion coefficients were similar in value. It was explained by identical dispersion of the sorbents samples and the similarity of the layered structure of clay minerals.

Adsorption isotherms models

The data of dependences of the SDBS and SLS adsorption by MCSp-7, MCSd-4 and MCP-7 samples of their residual equilibrium concentration $C$ were used for adsorption parameters calculations (Fig. 2).

The best fit of experimental data in the case of tested anionic SAs was obtained with the Langmuir model (Table 2). The theoretical maximum adsorption capacities of MCSp-7, MCSd-4 and MCP-7 calculated by Langmuir equation were good agreed with experimentally obtained values. Thereby, the monolayer adsorption of SDBS and SLS on the pores surface of magnetic composites was presented. So, the relatively uniform energy distribution of active adsorption sites on the pores surface of composites was achieved.

Adsorption thermodynamics

Van’t Hoff plots for SDBS and SLS adsorption by MCSp-7 ($R^2$ is 1.0 and 0.9996, respectively), MCScd-4 ($R^2$ is 0.9970 and 0.9989, respectively) and MCP-7 ($R^2$ is 0.9986 and 1.0, respectively) were obtained. The calculated activation energy of anionic SAs sorption by magnetic composites was approximately 5 kJ/mol, which confirmed the physical nature of the process. Furthermore, activation energy values lower than 42 kJ/mol indicated diffusion control processes (Eren, 2009). The increasing $\Delta G^0$ values with increasing temperature testified that the adsorption of SAs becomes unfavorable at higher temperature because the process does not require energy to take place.

The negative value of $\Delta H^0$ suggested that SDBS and SLS removal process by magnetic composites was exothermic. The $\Delta S^0$ values were found to be negative which suggests decrease in the randomness at the solid/solution interface during the SAs adsorption.

Conclusions

An effective magnetic composite sorbents MCSp, MCSd and MCP based on cheap mineral raw were created. The sorption capacities of obtained magnetic composites containing magnetite 4-7 wt.% towards SDBS and SLS were in 4 and 7 times respectively higher compared to the native clays and exceeded the sorption capacity of magnetic fluid in 2 times. Thus, the found synergistic effect was caused, in our opinion, with change of porous structure of natural clay minerals and stabilization of magnetite nanoparticles on their pores surface.

The use of magnetic composites based on spondyle clay was most appropriate for SDBS removal. For water treatment from SLS the application of composite sorbents based on palygorskite was the most profitable.

Sorption isotherms were best adjusted to the Langmuir model. This means that magnetic composite sorbents have a homogeneous surface. The adsorption of SDBS and SLS onto magnetic composite could be considered to fit pseudo-second order kinetics model. However, the adsorption process was limited in the internal diffusion field. Thermodynamic studies showed that anionic SAs adsorption was spontaneous and endothermic nature. Estimated thermodynamic parameters ($\Delta G^0$, $\Delta H^0$ and $\Delta S^0$) of SAs sorption by magnetic mineral sorbents indicated that the sorption process was physical.

Consequently, SDBS and SLS removal was occurred within a short time without secondary water pollution. Therefore, applying of magnetic composite sorbents is a promising direction in modern water purification. Thus, we obtained the cheap magnetic sorbents based on natural clays and magnetite by the easy way, which not only quickly separated from the solution by magnetic separation, but efficiently remove anionic surfactant substances at low concentrations.

Acknowledgments

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References


